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(54) NOVEL SULFUR-CONTAINING ALIPHATIC (METH)ACRYLATE

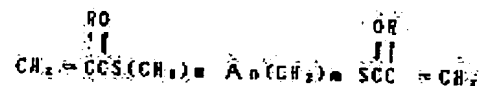
(57)Abstract:

NEW MATERIAL: The compound of formula (A is O or S; R is H or methyl; m is 1 or 2; n is 0 or 1).

EXAMPLE: 2,2'-Oxydiethanethiol diacrylate.

USE: Raw material for acrylic resin or methacrylic resin useful as an optical part such as lens.

PREPARATION: The objective compound of formula can be produced e.g. by adding 2W2.5mol of acryloyl chloride or methacryloyl chloride to 1mol of ethanedithiol 2,2'-oxydiethanethiol or 1,4-butanedithiol, etc., in a solvent (e.g. hexane, benzene, etc.), keeping the mixture at $-10W+30^{\circ}$ C, preferably $-10W+10^{\circ}$ C and reacting the components in the presence of a hydrochloric acid scavenger such as triethylamine. A resin having high refractive index and keeping high Abbe number can be produced by thermally polymerizing the compound of formula with an unsaturated carboxylic acid ester.



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English Translation of JP JP, 63-188660, A

* NOTICES *

1. This document has been translated by computer using translation software, PAT-Transer V7 produced by Cross Language Inc. So the translation may not reflect the original precisely.
2. The word which can not be translated is expressed by Japanese character.
3. The drawings and tables are not translated.

[Claims for the Patent]

[claim 1]

The 含硫脂肪族 (meta) acrylate which is presented in a general formula (I).

(during a ceremony, as for A, oxygen or sulfur, R show hydrogen or methyl group, as for m, 1 or 2, n are integers of 0 or 1.) But) which is 0 integers as for n as for m 2 in that case of methyl group R

[Detailed Description of the Invention]

(a field of industrial application)

The present invention is related to useful new 含硫脂肪族 (meta) acrylate as acrylic resin or raw materials of methacrylic resin.

(prior art:)

Ethylene glycol Zia chestnut rate, diethylene glycol dimethacrylate are utilized by property modification of acrylics and polymethacrylate resin namely bridging. (the problems that invention is going to solve)

People of present invention study that acrylic resin and methacrylic resin are utilized as resin for optical components such as lens use, but, as for the resin which can be done other bifunctional monomer and copolymerization in benzenethiol acrylate, β - naphthalene thiol methacrylate as one functional monomer again, decentralization of index of refraction in visible light is big (the number of Abbe is small), and utility value is small without can expect high index of refraction when ethylene glycol Zia chestnut rate and diethylene glycol dimethacrylate are used as bifunctional monomer.

(means to solve problems)

While people of present invention maintain dispersion small, investigation of 含

硫二官能性 monomer was performed zealously to get high resin of refraction index.

As a result, it is found that this purpose can be achieved by using 含硫脂肪族 (meta) acrylate, the present invention was led to.

In other words the present invention provides acrylic resin or 含硫脂肪族 (meta) acrylate presented in a useful new general formula (I) as raw materials of methacrylic resin.

(during a ceremony, as for A, oxygen or sulfur, R show hydrogen or methyl group, as for m, 1 or 2, n are integers of 0 or 1.) But) which is 0 integers as for n as for m 2 in that case of methyl group R.

As for the new 含硫脂肪族 (meta) acrylate of the present invention, ethanedithiol Zia chestnut rate, 2,2' - Oki ti diethanethiol Zia chestnut rate, 2,2' - チオジエタンチオールジアクリレート, 1,4- butane dithiol Zia chestnut rates and 1,4- butane dithiol dimethacrylate are exemplified to be concrete.

As for these compounds, it is got ethanedithiol, 2,2' - Oki ti diethanethiol, 2,2' - チオジエタンチオール or 1,4- butane dithiol and acrylic acid chloride or methacrylic acid chloride by performing esterification reaction in the presence of hydrochloric acid collector in solvent.

In other words a synthesis reaction adds acrylic acid chloride or two or more methacrylic acid chloride 2.5 mol for material ethanedithiol, 2,2' - Oki ti diethanethiol, 2,2' - チオジエタンチオール or 1,4- butane dithiol 1 mol among solvent, the solvent which, for example, do not have hexane, benzene, toluene, material such as chloroform and reactivity, and preferably it is kept, and 反応液温 -10 degrees Celsius - 30 degrees Celsius add the hydrochloric acid collector which seems to be triethylamine to -10 degrees Celsius - 10 degrees Celsius, and reaction can be gone ahead through. Subsequently a rare alkali water solution is water, and reaction liquid is washed, and, after reaction termination, removal assumes solvent, and 含硫脂肪族 (meta) acrylate of the present invention can be got.

(operation)

While 含硫脂肪族 (meta) acrylate of the present invention is compared with resin with the use of conventional diethylene glycol Zia chestnut rate and ethylene glycol Zia chestnut rate by or polymerizing heat with unsaturated carboxylic ester such as diethylene glycol dimethacrylate, ethylene glycol dimethacrylate alone, and maintaining high Abbe number, 含硫 acrylic resin having high index of refraction or 含硫 methacrylic resin can be got, it is useful for optical components.

(an example)

It is shown to that example as follows, but a department of the whole example shows part by weight.

Example 1

While nine parts of 2,2'-Oki ti diethanethiol, chloroform 200 parts, acrylic acid chloride 13.6 parts are mixed, and keeping 反応液温 -5 degrees Celsius, 15.4 parts triethylamine could be written for 35, and drip was done. After, after drip termination, having washed with 5% sodium hydrogen carbonate water solution, water was washed, and the chloroform layer was concentrated. Concentrate was refined by chromatogram method, and three parts of 2,2'-Oki ti diethanethiol Zia chestnut rates of form of colorless syrup were got.

48.42 6.03 25.45 CHS ultimate analysis value (%) calculated value (%) 48.76 5.73 26.03 (as C₁₀H₁₄O₃S₂)

Example 2

While nine parts of 2,2'-チオジエタンチオール, chloroform 200 parts, acrylic acid chloride 12.2 parts are mixed, and keeping 反応液温 -5 degrees Celsius - 0 degrees Celsius, 13.8 parts triethylamine could be written for 30, and drip was done. After, after drip termination, having washed with 5% sodium hydrogen carbonate water solution, water was washed, and the chloroform layer was concentrated. Concentrate was refined by chromatogram method, and 3.6 parts 2,2 colorless syrup-shaped ' - チオジエタンチオールジアクリレート was got.

45.26 5.62 37.11 CHS ultimate analysis value (%) calculated value (%) 45.77 5.38 36.66 (as C₁₀H₁₄O₂S₃)

Example 3

2.5 parts ethanedithiol Zia chestnut rates of act form of colorless syrup were got same as example 1 except that nine parts of 2,2'-Oki ti diethanethiol of example 1 was exchanged with 6.1 parts ethanedithiol.

Nine parts of 2,2'-Oki ti diethanethiol of 47.79 5.02 31.59 47.50 4.98 31.70 (as C₈H₁₀O₂S₂) 5.70 (m, 2H, CH₂=CH-) 6.30 (m, 4H, CH₂=CH-) four CHS ultimate analysis value (%) calculated value (%) NMR δ (CDCl₃) δ =3.50 (s, 4H, -SCH₂CH₂S-) example example 1 was performed same as example 1 except that 13.6 parts acrylic acid chloride was exchanged with 14.1 parts methacrylic acid chloride in 7.9 parts 1,4- butane

dithiol, and 3.1 parts 1,4-butane dithiol dimethacrylate of form of colorless syrup was got.

55.50 7.13 24.95 CHS ultimate analysis value (%) calculated value (%) 55.78 7.02 24.82 (as C₁₂H₁₈O₂S₂)

Example 1

54 parts of 2,2'-Oki ti diethanethiol Zia chestnut rates, diethylene glycol dimethacrylate six parts and 0.01 parts lauroyl peroxide were mixed, and uniformity and the fluid which did were poured by the end of mold pattern constructed as in a glass mold and gasket comprising ethylene-vinyl acetate copolymer. Subsequently temperature was raised slowly polymerization was begun at 30 degrees Celsius at first, and to become 70 degrees Celsius six hours later. Furthermore, polymer has begun to be taken out of the aftergas blanket which polymerized at 80 degrees Celsius for two hours and a mold. The polymer polymerized at 90 degrees Celsius more for two hours. This polymer was refraction index 1.58, number of Abbe 37, and processing characteristics, chip resistance were good with colorless transparency, too.

In addition, the refraction index and the number of Abbe measured at 20 degrees Celsius at プルリッヒ type refraction index. In addition, face processing characteristics grinds by ball woodcut print airplane for glasses lens processing, and to grind does a good thing with Ryo (○), the thing which blocking is waked up, and cannot be ground is done with defectiveness (×), the thing which a center thickness used a flat sheet of 2mm as chip resistance, and, therefore, steel sphere drop test was performed in FDA specification, and cannot be broken was done with Ryo (○).

Example 2

40 parts of 2,2'-チオジエタンチオールジアクリレート, ethylene glycol dimethacrylate ten parts and 0.01 parts ジクミールパーオキサイド were mixed, and uniformity and the fluid which did were poured by the end of mold pattern constructed as in a glass mold and gasket comprising ethylene-vinyl acetate copolymer. Subsequently temperature was raised slowly polymerization was begun at 30 degrees Celsius at first, and to become 70 degrees Celsius six hours later. Furthermore, polymer has begun to be taken out of the aftergas blanket which polymerized at 80 degrees Celsius for two hours and a mold. The polymer polymerized at 90 degrees Celsius more for two hours. This polymer was refraction index 1.61, number of Abbe 36, and processing characteristics, chip resistance were good with colorless

transparence, too.

Example three or four

It was performed same as example 1 except that 54 parts of 2,2' - Oki ti diethanethiol Zia chestnut rates of example 1 were exchanged with 54 parts of 1,4-butane dithiol Zia chestnut rates or 54 parts of 1,4-butane dithiol dimethacrylate respectively, and polymer was got.

Example 5

Act polymer was got same as example 2 except that 40 parts of 2,2' - チオジエタンチオールジアクリレート of example 2 was exchanged with 40 parts of ethanedithiol Zia chestnut rates.

Comparative example 1

It was performed same as example 1 except that independent, 60 parts of diethylene glycol Zia chestnut rates exchanged six parts of diethylene glycol dimethacrylate with 54 parts of 2,2' - Oki ti diethane Zia chestnut rates of example 1, and polymer was got.

Comparative example 2

It was performed same as example 2 except that 40 parts of 2,2' - チオジエタンチオールジアクリレート of example 2 and ethylene glycol dimethacrylate ten parts were exchanged with 30 parts of benzenethiol acrylate and ethylene glycol Zia chestnut rate 30 parts, and polymer was got. Refraction index, the Abbe number of these polymer, processing characteristics and a test result of chip resistance are shown to an outside front cover.